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Effects of solid pre-treatment towards optimizing supercritical methanol extraction and transesterification of *Jatropha curcas* L. seeds for the production of biodiesel

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ABSTRACT

Experimental studies for in situ extraction and transesterification of oil seeds had been carried out recently for the process intensification of biodiesel production. As opposed to the conventional method, the solid oil seeds would be in direct contact with the transesterification reagent. Both the oil extraction and subsequent transesterification process to biodiesel will occur simultaneously. Consequently, solid pre-treatments would play a critical role to ensure that the oil seeds are in a state for optimal oil extraction. Apart from obtaining a higher yield, this could also ensure that the oil extraction phase would not bottleneck the entire in situ extraction and transesterification process. However, solid pre-treatments could be both cost and energy intensive and therefore should be carefully selected for optimum advantages. In this experimental work, ground *Jatropha curcas* L. seeds were subjected to pre-treatments processes including de-shelling, sieving, drying and heat treatment at five different temperatures (45–105 °C) and two different durations (12 and 24 h) before undergoing single-step supercritical methanol extraction and transesterification. Conventional two-step extraction and transesterification was also performed as comparison to the single-step process. The effects of each pre-treatment were analyzed and optimized towards two responses (extraction and FAME yield). The highest extraction and FAME yield for the two-step and single-step processes were 66.82% w/w, 114.87% w/w and 68.50% w/w, 128.78% w/w respectively. Single-step supercritical methanol extraction and transesterification was found to be able to provide a higher extraction and FAME yield for the production of biodiesel with less pre-treatment stages and intensity as compared to the conventional two-step process. Therefore, this is a highly promising approach to reduce the high biodiesel production cost which is currently impairing the industry.

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1. Introduction

The availability and security of energy sources are two critical issues to be dealt with to meet the exponential-growing world energy demand brought by the increasing population. While current energy sources are still dominated by non-renewable fossil fuels such as coal and petroleum, renewable energy are widely believed to make more significant impact in the future energy demand particularly biomass-derived liquid biofuels. Various countries had slated to enforce mandatory minimum blending of biofuels (biodiesel and bioethanol) in their respective energy mix to reduce greenhouse gas (GHG) emissions and comply with sustainable development. However, current practices and processing technology of 1st generation biofuels from edible sources are deemed as unsustainable and competing with food and water supply which are already in high demand [1]. Moreover, most of the edible feedstock are expensive and often constituted over 70% of the total biodiesel production costs. Therefore, non-edible biofuel sources such as Jatropha have become the primary focus of research to overcome the challenges posed in current biofuels production. *Jatropha curcas* L. is a relatively obscure wild plant which can grow in semi-arid climates and harsh agricultural conditions. It can produce 2–5 tons of dry seed/ha/year with 30–35% oil by weight which can then be converted into biodiesel to replace mineral diesel as fuel in compression–ignition (CI) engines [2]. However, contemporary commercial production of biodiesel using alkaline transesterification is not efficient to utilize non-edible feedstock as most of them contained high moisture and free fatty acid (FFA) content [3]. Side-reactions such as saponification will inhibit the transesterification process and thus provide lower biodiesel yield and quality. Consequently, various researches in energy intensive countries had been carried out to discover more cost-effective production routes for Jatropha-based biodiesel.

Conventional method for the production of biodiesel from Jatropha are either acid-catalyzed or two-step acid–base catalyzed transesterification processes [4–6]. Non-catalytic supercritical

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fluid process utilizing methanol and dimethyl carbonate has also being successfully developed for the production of Jatropha biodiesel [7,8]. However, most of the processes will first have to undergo oil extraction phase in order to extract the triglycerides from the oil seeds [9]. Oil extraction phase involves several stages such as cleaning, dehulling, drying and grinding. The extracted oil will then be subjected to various purification processes such as degumming, dewaxing and deacidification before being converted to biodiesel. These multiple processes are responsible for a significant portion of the overall biodiesel processing cost [10]. Besides, they require a larger amount of chemicals and energy while at the same time generate more waste streams. Recently, in situ extraction and esterification/transesterification or also known as reactive extraction has shown promising results as an efficient method to produce fatty acid methyl esters (FAME) [10–12]. Reactive extraction enables the oil-bearing solid biomass to be in contact directly with short-chain alcohol instead of pre-extracted oil. Extraction and transesterification will proceed simultaneously with alcohol acting both as an extraction solvent and a transesterification reagent. By removing the requirement for two separate processing phases, it can greatly reduce both the processing time and cost. Nevertheless, catalytic reactive extraction is still faced with challenges such as slow reaction rate and complex catalyst separation. In our previous preliminary study, non-catalytic supercritical reactive extraction of *J. curcas* L. seeds had been proven to be highly feasible to produce biodiesel with the absence of several drawbacks from catalytic reactive extraction [13]. However, it was found that both the rate and total amount of oil extracted from the oil seeds during the supercritical methanol reactive extraction played an important role in optimizing the overall yield of FAME for the subsequent esterification and transesterification processes. Therefore, it is imperative for the solid oil seeds to be subjected to certain pretreatment processes for maximum oil recovery. This will also ensure that the oil extraction phase will not bottleneck the entire process and thus leads to higher product yield. Despite these facts, solid pre-treatment processes are highly energy-intensive and optimization should be carried out in order to maintain economic competitiveness of biodiesel [14,15].

In this study, the effect of different solid pre-treatments (drying, sieving and de-shelling) will be investigated on ground *J. curcas* L. seeds for the FAME production using supercritical methanol reactive extraction. Their direct influence towards the process extraction efficiency and final FAME yield will be analyzed. Comparison will also be made with conventional two-step extraction and transesterification process to determine the relative difference between the two processes. Currently, there are only few literatures available pertaining to the oil extraction efficiency of supercritical methanol. Hence, it is hope that this study will serve as a good reference for future research and development work on supercritical fluids reactive extraction process.

2. Experimental

2.1. Materials

J. curcas L. seeds used in this study were purchased from a local plantation company in Malaysia. Methanol of 99.8% purity was purchased from HmbG Chemicals, Germany. Analytical grade *n*-hexane of 99% purity (Merck, Germany) was used in Soxhlet oil extraction and as co-solvent in the supercritical reactive extraction. Methyl heptadecanoate (99.5% purity) as internal standard and standard references for methyl esters which include 99% methyl palmitate, 99% methyl stearate, 99% methyl oleate and 99% methyl linoleate were all obtained from Fluka Chemie, Germany for gas chromatography (GC) quantification.

2.2. Pretreatment of Jatropha curcas L. seeds

Fresh *J. curcas* L. seeds were first manually screened in which only good-condition seeds were selected while damaged seeds were being discarded to ensure higher uniformity of experimental results. The seeds were first grounded using a mechanical grinder (Moulinex, France). For seeds de-shelling analysis, the seeds were manually de-shelled by using pliers to obtain the seed kernels (white shelled nut) prior to the grinding. Afterwards, grounded seeds will be subjected to heat treatment by drying in a vacuum oven (Memmert D-91126, Germany) at 45, 60, 75, 90 and 105 °C for 12 and 24 h. Drying under vacuum condition can prevent surface reaction such as oxidization of the oil seeds with the air. After drying, the Jatropha samples were then screened using a vibrator sieve shaker (Retsch, Germany). It was important to dry the seeds first before sieving as wet seeds were more likely to be sticky and thus might render sieving process to be ineffective. The sieving period was 15 min and solid particle size fraction of $\leqslant 1.0$ mm was collected and stored in a desiccator to prevent absorbing moisture. Moisture content of grounded samples (15 g of sample size) at different heat treatment temperature and duration was determined based on their wet weight basis which was calculated by placing in the same oven at determined temperature repeatedly until constant weight was achieved using electronic balance (Shimadzu AC220, Japan). Each measurement was carried out in triplicates and the yields are found to agree within 5%.

$$\text{Moisture content}, M_{\text{wet}} = \frac{\text{Initial weight (g)} - \text{Final weight (g)}}{\text{Initial weight (g)}} \times 100\% \tag{1}$$

2.3. Oil extraction

Grounded, dried and sieved seed samples were subjected to Soxhlet extraction using *n*-hexane to determine the total oil content extractable through chemical extraction method. 15 g of the seed samples was weighed and poured into a 30 mm × 100 mm cellulose extraction thimble. The filled thimble would be loaded inside a 125 ml Soxhlet extractor with 200 ml *n*-hexane as extraction solvent. The extraction was performed for 24 h to ensure complete oil extraction with solvent to solid ratio (SSR) fixed at 800. The solvent containing the extract was then filtered to remove other solid contaminants and evaporated with rotary evaporator (Buchi R-114, Switzerland) to remove the solvent. The remaining extract was then heated on a stirring hot plate for 1 h to remove any remaining *n*-hexane. Lastly, the extract was measured and weighed to record its volume and weight using the same electronic balance. Each measurement was carried out in duplicates and the yields are found to agree within 5%.

$$\text{Extraction yield}, M_{\text{extract}} = \frac{\text{Weight of extract (g)}}{\text{Weight of feed (g)}} \times 100\% \tag{2}$$

2.4. Two-step extraction and transesterification

After the extraction phase, the oil would undergo transesterification process using acidic homogenous catalyst as described in the literature [9]. All the amount of oil obtained from each batch of seed samples by Soxhlet extraction was loaded into a 500 ml round-bottom flask equipped with a reflux system on a stirring hot plate. Methanol as the transesterification reagent and concentrated H_2SO_4 as the homogenous acidic catalyst were then added according to the optimization conditions stated in the literature [10]. Reaction temperature was fixed at 60 °C and the reaction proceeded under constant stirring for 10 h before being cooled upon completion. The products were then evaporated in a rotary evaporator to remove excess methanol. The remaining liquid product was allowed to be settled overnight by gravity in a separation funnel. Two layers of liquid would be formed with the top layer containing FAME-rich phase in dark yellow color while the bottom layer contained glycerol-rich phase in dark brown color. The bottom layer was decanted off while the volume and weight of the top layer was then measured and recorded.

2.5. Supercritical methanol extraction and transesterification

Pretreated solid *J. curcas* L. seeds were subjected to supercritical methanol extraction and transesterification process in a high pressure batch reactor as described in the literature [16]. For each experimental run, 15 g of ground seeds would be loaded into the 450 ml reactor along with 200 ml methanol and 50 ml *n*-hexane. Hexane was required to increase the oil extraction rate and its solubility in the reaction mixture. It would also help to facilitate the separation of FAME from glycerol in the final product [13]. Mechanical agitation was set at a speed of 400 rpm and started as soon as heating commenced. Final reaction temperature was fixed at 300 °C for 30 min before quenching with cooling water immediately to room temperature. Afterwards, the reaction mixture was filtered and washed thrice with 30 ml *n*-hexane to remove remaining solid residues. The liquid product was then stirred with 100 ml *n*-hexane for 30 min before transferred into separating funnel. Two visible layers would be formed after settling by gravity for 1 h. The top dark yellow layer which was rich in FAME and *n*-hexane would be decanted and evaporated in rotary evaporator to remove the solvent. The separation procedure was repeated twice for the bottom layer to recover remaining FAME. The volume and weight of the total collected FAME was then measured and recorded as total extract from supercritical reactive extraction. Each measurement was carried out in triplicates and the yields are found to agree within 5%.

2.6. Product analysis

The final FAME samples were then analyzed by using gas chromatography (GC) (Perkin–Elmer, Clarus 500) equipped with a Nukol™ capillary column (15 m × 0.53 mm; 0.5 μm film thickness) and a flame ionization detector (FID) to obtain their composition and yield. Helium gas was used as the carrier gas in the GC. The initial temperature of the oven was set at 110 °C for 0.5 min and then increased to 220 °C for 8 min at the rate of 10 °C/min. The temperatures of the injector and detector were set at 250 °C and 220 °C respectively. Each FAME sample was diluted with *n*-hexane as the solvent and methyl heptadecanoate as the internal standard before injected into the column with 1.0 μl volume for each injection. Peaks of different methyl esters in the FAME samples were identified by comparing the retention time of each component in the sample chromatogram with the peaks of pure methyl ester standard compounds. The yield of FAME was then calculated according to the equation shown below. Average weight of oil extractable from Jatropha seeds determined from the literature in the equation 3 below was 54.36 wt.% [17].

$$\text{FAME yield, } F_Y = \frac{(\sum \text{concentration of each methyl esters})\ (\text{g/ml}) \times (\text{volume of FAME})\ (\text{ml})}{\text{Average weight of oil extractable from literature (g)}} \times 100\% \qquad (3)$$

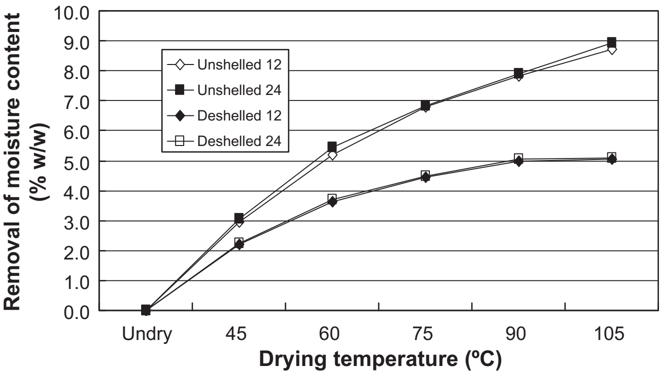

Fig. 1. Total removal of moisture content from ground Jatropha seeds at different drying temperature and duration.

3. Results and discussion

3.1. Moisture content

Fig. 1 shows the total removal of moisture content on a wet basis from ground Jatropha seeds subjected to different drying temperatures (45 °C, 60 °C, 75 °C, 90 °C and 105 °C) under vacuum oven. Four different samples (de-shelled and unshelled) with drying time (12 and 24 h) were studied. It was noted that total moisture content in the samples based on the standard 105 °C wet weight basis were 8.94 wt.% and 5.11 wt.% for unshelled and de-shelled samples respectively. The amount of moisture lost was almost similar with the values reported in other literatures [17,18]. De-shelling ground Jatropha seeds can successfully eliminate about 42.8% of moisture content in original seeds. Drying time was discovered to have almost negligible effect to the total removal of moisture content from ground Jatropha seeds. From Fig. 1, there is almost no difference between drying time of 12 and 24 h. Further investigations on the drying time found that almost 95% of the final moisture content in Fig. 1 was removed within 1 h for all 5 drying temperatures (results not shown). Drying temperature played a more dominant effect towards the final moisture content of the seeds especially at the lower end (45 °C and 60 °C). The decreasing gradient shown in Fig. 1 proved that less moisture was being removed as drying temperature increased. This could be explained through the drying mechanism of ground Jatropha seeds. Initially, evaporation of water will occur from the surface and outer regions. As drying progresses, water content further inside the parenchymal cells within the seed's organic structure will need to be transported to the surface before being evaporated [19,20]. The deeper the water molecules trapped inside the structure, the higher amount of energy will be needed (critical energy) for their transportation to surface and subsequent evaporation. Higher drying temperature can provide the necessary amount of critical energy required to transport water molecules inside the seed's core to the surface within a short timeframe (1 h) before being evaporated. Longer drying time is only required to evaporate more water molecules from the surface and does not contribute effectively to the critical energy required for the transportation. Since the total removable moisture content of the ground Jatropha seeds was small (<10 wt.% for unshelled seeds and <6 wt.% for de-shelled seeds), the required drying time was short and therefore would not play an important role in this study. Moreover, the grounded seeds had larger surface areas which accelerated the surface evaporation.

At 105 °C drying temperature, the gradient for de-shelled ground seeds was almost reaching zero. This means that drying temperature at 90 °C or 105 °C was able to evaporate most of the moisture content inside the seed's kernels due to the absence of hardened shell. It should also be noted that high drying temperature might destroy the biomass surface which would obstruct transportation of the moisture to the surface. Hence, further increment of the drying temperature might not be able to remove more water molecules effectively. In contrary, ground seeds with shell intact still contained removable moisture content even when drying at above 105 °C. This might be due to the thicker cellulose and lignin shell which will impede the transportation of water molecules to the surface [21]. Therefore, higher drying temperature will be required to overcome the higher critical energy barrier to remove the water molecules in moisture-rich Jatropha shells. Consequently, heating temperature played a more significant role towards the removal of moisture content for virgin ground seeds (un-sieved, undry and not shelled). However, drying temperature higher than 105 °C might not be economically feasible since it will consume huge amount of energy especially for large-scale production. Since Jatropha seeds are also rich in lipids, volatilization of light hydrocarbons or fatty acids might also occur which added to the total weight loss.

3.2. Oil yield and efficiency

Figs. 2 and 3 show the total amount of extraction contents after undergoing heat treatment at different temperatures for un-sieved and sieved (⩽1.0 mm fraction) ground seeds respectively without de-shelling. Extraction yields from conventional two-step soxhlet extraction (SE) and supercritical reactive extraction (RE) were compared with heat treatment duration of 12 and 24 h. Average oil yield of ground Jatropha seeds determined from the literature was 54.36 wt.% and included in the figures for comparison purpose [17].

All four trend lines shown in Fig. 2 register extraction contents less than the average value from the literature which suggested that un-sieved ground seeds were not optimal for oil extraction. In overall, heat treatment on the seeds prior to oil extraction had a substantial effect to the final extraction yield. As shown in Fig. 2, there existed an optimum heat treatment condition for maximum oil extraction. For SE, the optimum heat treatment condition (60 °C for 12 h) can increase the extractable oil content up to 30.3%. Similarly for RE, an increment of 33.0% for oil yield at 90 °C for 12 h can be achieved compare to untreated ground seeds. Heat treatment at mild drying temperature could improve biomass microstructure such as pores and surface area which in turn mediated oil or lipid extraction in higher efficiency. This was then added onto the effect of reduced moisture content due to evaporation. However, higher drying temperature also had the possibility to destroy the molecular bonds and structures which will be detrimental not only towards the extraction yield but also the quality of the oil [22]. Therefore, it was important to determine the optimum drying temperature for heat treatment of Jatropha seeds. Extraction yields for both SE and RE at 12 and 24 h were almost similar below 60 °C drying temperature. Beyond that, extraction contents for SE at 12 and 24 h heat treatment started to decrease with increasing drying temperature. This suggested that the changes in the biomass microstructure were no longer favorable towards hexane soxhlet extraction even with more moisture content being removed. Meanwhile, higher drying temperature for heat treatment was still proven to be beneficial for supercritical reactive extraction. Both RE 12 h and 24 h exhibited increasing extraction yield with increasing drying temperature. Nevertheless, after the optimum drying temperature for RE 24 (75 °C) and RE 12 (90 °C), the total amount of extraction contents started to decrease too. The difference between heat treatment duration of 12 and 24 h began to be noticeable at higher drying temperature. The sharp drop in the extraction yield for SE 24 h compare to SE 12 h implied that prolong exposure to higher than optimum drying temperature would be counter-productive for oil extraction. Likewise, extraction yield for RE 24 h dropped more than RE 12 h after the optimum temperature. This might be due to the destruction of biomass surface at higher temperature which was similar to the biomass torrefaction process and thus obstructing extraction in supercritical reactive extraction [23].

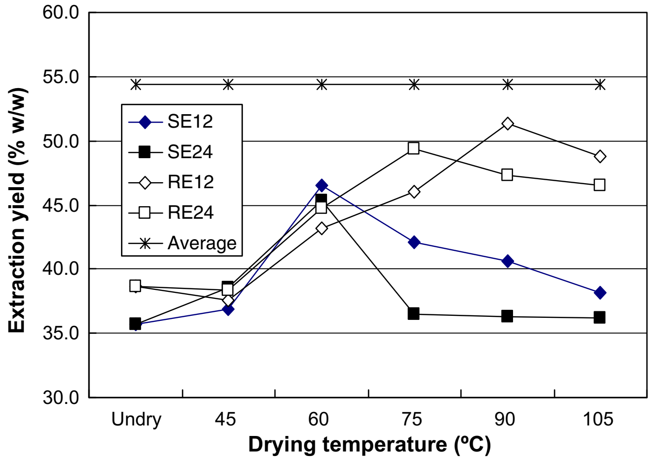

Fig. 2. Extraction yield for SE and RE processes at different drying temperature and duration for un-sieved ground Jatropha seeds (with shell).

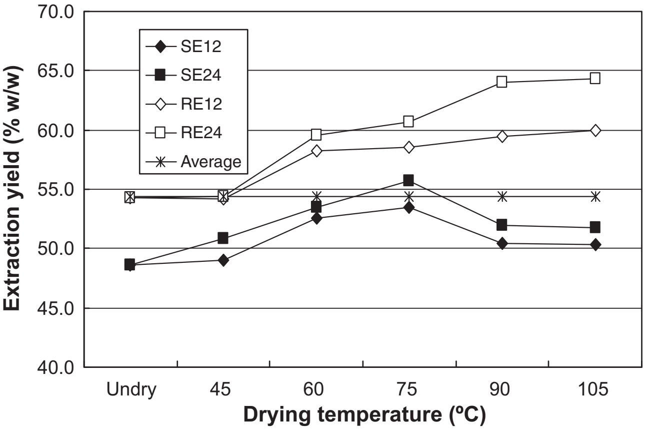

Fig. 3. Extraction yield for SE and RE processes at different drying temperature and duration for sieved ground Jatropha seeds (with shell).

Fig. 3 shows the extraction yield for sieved ground Jatropha seeds with ⩽1.0 mm particle size fraction. The results were distinctively very much different from Fig. 2. All of the results recorded in Fig. 3 were higher than their counterparts in Fig. 2. This confirmed the fact that smaller particle seeds could promote higher extraction yield with the same drying and heat treatment condition [12]. Even though in general, increasing drying temperature will still increase the extraction yield for both RE and SE extraction processes, the increment recorded was lower compare to un-sieved Jatropha seeds. For SE and RE, at the optimum or maximum heat treatment condition (75 °C and 105 °C for 24 h), the extraction amount only increased by 14.6% and 18.5% respectively. This might be due to the high extraction yield already being extracted out for smaller particle size of Jatropha seeds. As most of the extractable content had been extracted out, significant improvement might be difficult. Both SE 12 and 24 h exhibited optimum condition before experiencing a sharp drop with increasing drying temperature as in un-sieved seeds. However, the extraction yields for RE 12 and 24 h did not show any optimum condition and will most probably continue to increase beyond the maximum drying temperature in study. The shifting of optimum condition to higher drying temperature proved that smaller particle sizes were less susceptible to heat treatment. This had also lead to the results that drying at longer hours (24 h) had higher oil yield than at 12 h as opposed to the results in Fig. 2. Thus, smaller particle sizes will be more favorable for reactions associated with high temperature as they had a smaller volume to surface area ratio. Consequently, any surface transformation will pose less resistance towards the oil extraction mechanism.

All extraction yields from RE 12 and 24 h show equal or higher than average oil content from the literature while only SE 24 at the optimum heat treatment condition was higher than 54.36 wt.%. This shows the potential of supercritical reactive extraction over conventional oil extraction for biodiesel production. Comparison of extraction efficiency between the two processes was done through Eq. (4) and shown in Fig. 4. Higher value of comparison extraction efficiency will represent better performance of supercritical reactive extraction (RE) over conventional two-step extraction and transesterification (SE) in terms of extraction yield.

Comparison extraction efficiency,

$$E_e = \frac{\text{Mass of extract from RE (g)}}{\text{Mass of extract from SE (g)}} \times 100\% \tag{4}$$

With 100% as the minimum benchmark, only un-sieved ground Jatropha seeds at 60 °C and 45 °C registered lower or equal than the baseline comparison extraction efficiency. This was due to the optimum condition of extraction yield from conventional soxhlet extraction as mentioned earlier. As drying temperature progressed, comparison extraction efficiency increased which proved the superiority of supercritical reactive extraction after undergoing heat treatment. The maximum E_e occurred at 75 °C 24 h for un-sieved ground seeds. This was resulted from the sharp drop of oil yield from SE due to excessive heat treatment. Nevertheless, higher amount of oil content can be extracted from sieved ground seeds despite lower E_e and therefore should be taken into consideration as well for optimal biodiesel production. For sieved ground seeds, comparison extraction efficiency remained almost constant at lower drying temperatures. As drying temperatures increased beyond 75 °C, E_e for both 12 and 24 h increased substantially. Therefore, at high drying temperature, supercritical reactive extraction would generally perform better than conventional soxhlet extraction during extraction processes.

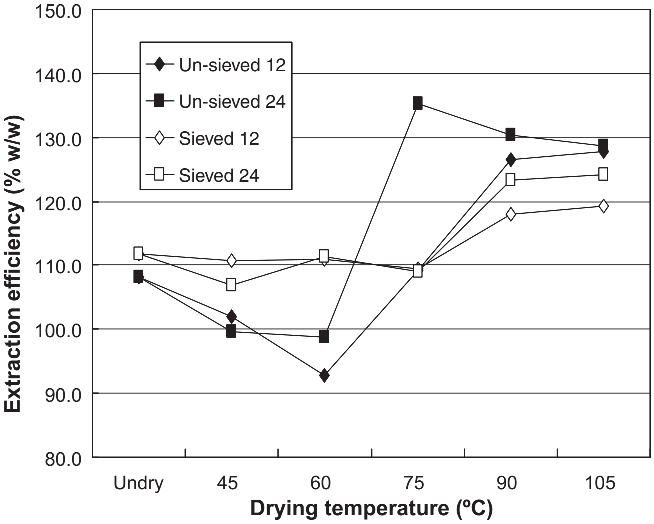

Fig. 4. Comparison extraction efficiency for un-sieved and sieved ground Jatropha seeds at different drying temperature and duration (with shell).

3.3. FAME yield and efficiency

Figs. 5 and 6 depict the FAME yield for un-sieved and sieved ground Jatropha seeds respectively for SE and RE at both 12 and 24 heat treatment duration. From the results of GC, there were four identified primary peaks which corresponded to the four fatty acids in Jatropha oil: methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Even though their compositions vary for each experimental run, nevertheless methyl linoleate always remain as most abundant component; followed by methyl oleate, methyl palmitate and lastly methyl stearate for both SE and RE processes (results not shown). This proved that the chemical composition of the fatty acids in extracted Jatropha oil would not be greatly affected even in supercritical condition due to thermal decomposition or pyrolysis as initially feared. From Fig. 5, increasing drying temperature and duration did not seem to have significant effect towards the FAME yield of SE process. Even though the

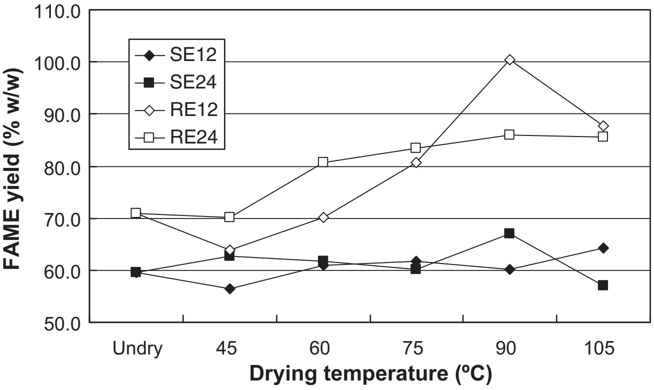

Fig. 5. FAME yield for SE and RE processes at different drying temperature and duration for un-sieved ground Jatropha seeds (with shell).

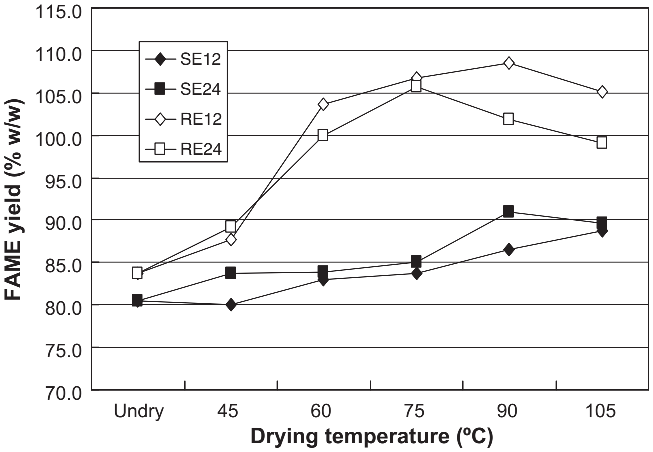

Fig. 6. FAME yield for SE and RE processes at different drying temperature and duration for sieved ground Jatropha seeds (with shell).

extract yield increased, the amount of triglyceride extracted did not increase in tandem. This is rather un-expected because there is an increase in the extraction yield with increasing drying temperature. One possible explanation for this is that most of the extracts which had been extracted out due to the increasing drying temperature consist of non-fatty acids such as hydrocarbons and other lipids. In other words, there are still a lot of fatty acids (including triglycerides and free fatty acids) still entrapped inside the seeds since un-sieved ground seeds had a much smaller surface area for effective extraction. In contrary, FAME yields for RE process increase in tandem with the trend shown for their corresponding extraction yields. Increasing drying temperature will help to increase the amount of fatty acids been extracted out and subsequently increased the overall FAME yield. The optimum FAME yield occurred at 90 °C for RE 12 which was the same as the optimum extraction yield. Therefore, it can be concluded that fatty acids extraction can benefit from the increasing drying temperature for supercritical reactive extraction. The high temperature and pressure involved in RE will help to extract out more entrapped fatty acids (triglycerides and free fatty acids) as compare to SE. When undergoing higher drying temperature than the optimum, the reduction in extraction efficiency will also affect the total amount of FAME yield at the end. This might be due to less fatty acids being able to be extracted out due to surface morphology changes from the heat treatment. The gradient of FAME yield for RE 24 was also approaching zero which reflected that the maximum extractable fatty acids at that pre-treatment condition had almost been reached.

Fig. 6 shows the FAME yield for both SE and RE processes for the duration of 12 and 24 h on sieved ground Jatropha seeds ($\leqslant$1.0 mm particle size fraction). As with the case of un-sieved ground seeds, FAME yield for SE 12 and 24 h in Fig. 6 did not show much increment at the lower range despite increasing drying temperature. However, the increment becomes more significant at higher drying temperature beyond 75 °C even though their corresponding extraction yield decreased. Since sieved ground seeds had a higher surface area per volume, entrapped fatty acids had a much lower mass transfer resistance and therefore will benefit much more from increasing heat treatment temperature. At higher drying temperatures, the destruction of surface molecular structure reduced the overall extraction yield but more fatty acids had been successfully extracted. This might be due to the smaller molecular sizes of the fatty acids compare to the other lipids which still enabled them to be extracted out easily albeit only in a small quantity. In contrary, FAME yields for RE process exhibited larger responses to increasing drying temperature. Both RE 12 and 24 h had achieved more than 100% of FAME yield compare to the average FAME yield of Jatropha found from the literature starting from 60 °C drying temperature onwards. This showed that supercritical reactive extraction was promising as a high yield biodiesel production method. At low drying temperatures, the increment of FAME yields were in tandem with increment of extraction yield which means more amount of fatty acids were being successfully extracted out. However, closer observation at high drying temperatures showed that FAME yield decreases slightly even though extraction efficiency continues to rise. This was probably due to the losses of fatty acids which underwent volatilization due to the high temperature and reduced mass transfer resistance. Moreover, the saturation point for fatty acids extraction had been reached and therefore will be difficult to increase further. The reduction was not detectable by the trend shown by SE process because their FAME yield was still low to reach the maximum extraction limit.

Fig. 7 shows the calculated comparison FAME efficiency from Eq. (5). This value will serve as a direct efficiency comparison between the two processes (RE and SE) for the extraction of fatty acids and subsequent esterification/transesterification to produce biodiesel. Higher value of comparison FAME efficiency will represent better performance of supercritical reactive extraction (RE) over conventional two-step extraction and transesterification (SE) in terms of biodiesel yield.

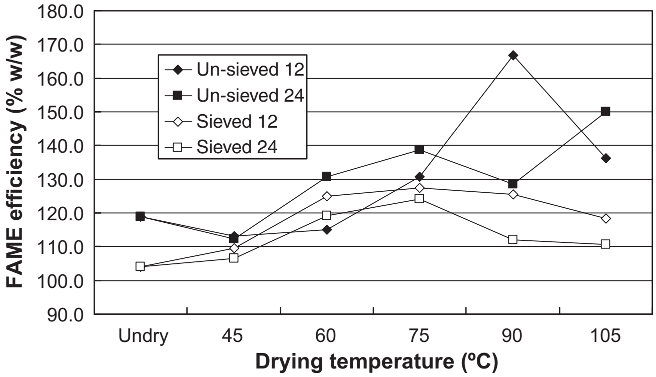

Fig. 7. Comparison FAME efficiency for un-sieved and sieved ground Jatropha seeds at different drying temperature and duration (with shell).

Comparison FAME efficiency,

$$F_e = \frac{\text{Total mass of FAME for RE (g)}}{\text{Total mass of FAME for SE (g)}} \times 100\% \tag{5}$$

All of the comparison FAME efficiency was higher than 100% which again suggested that fatty acids extraction for supercritical reactive extraction was superior compare to the conventional two-step extraction and transesterification. In general, F_e increased with increasing drying temperature. Sieved ground Jatropha seeds showed a more subtle F_e changes over increasing drying temperature with the optimum at 75 °C for both 12 and 24 h drying duration. In terms of efficiency and total amount of FAME, 12 h drying duration proved to be slightly more superior to 24 h at all drying temperatures. On the other hand, un-sieved ground Jatropha seeds exhibited more significant changes with the highest comparison FAME efficiency at 166.75% w/w for 12 h drying time. This was largely due to the huge increment of FAME yield as recorded in Fig. 5 at 90 °C. Furthermore, un-sieved ground Jatropha seeds had a higher irregularity in terms of extraction and FAME yield. While high F_e was desirable as portrayed by un-sieved ground seeds, sieved ground seeds still had a higher average amount of FAME yield and will have to be taken into account as well.

3.4. Effect of de-shelling

Based on the previous results and observations, drying duration of 12 h was adequate to cater for the moisture removal and also for the necessary solid heat treatment. High extraction and FAME yield can be attained in numerous pretreatment conditions shown above. In several occasion where drying duration of 24 h showed higher results, the difference was not large and sometimes negligible. Moreover, drying at 12 h could save more time, energy and ultimately cost. Therefore, drying duration of 12 h will be fixed for the seeds de-shelling experimental study below. Fig. 8 shows the extraction yield for un-sieved and sieved ground Jatropha seeds undergoing both SE and RE processes. It can be easily noticed that decorticated seeds had a much higher extraction yield compare to their corresponding un-shelled ground seeds and also the average literature value. This proved that the shell imposed a high mass transfer resistance towards the extraction process without containing significant amount of valuable extracts itself. Un-sieved ground Jatropha seeds were found to have a low extraction yield before heat treatment. As drying temperature increased, the

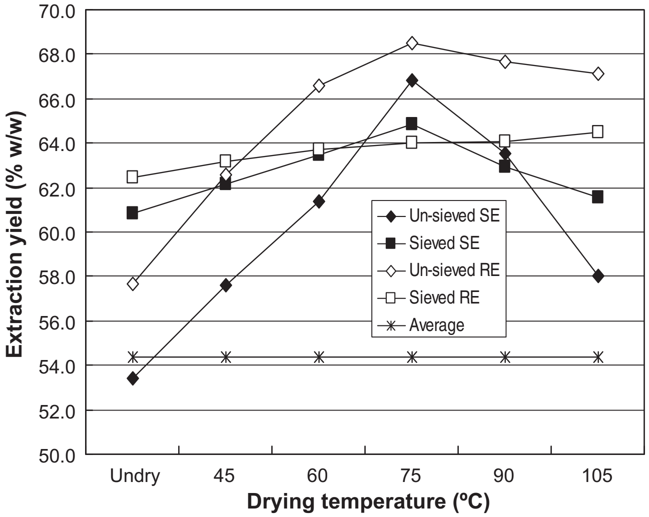

Fig. 8. Extraction yield for SE and RE processes at different drying temperature for sieved and un-sieved ground Jatropha seeds (de-shelled).

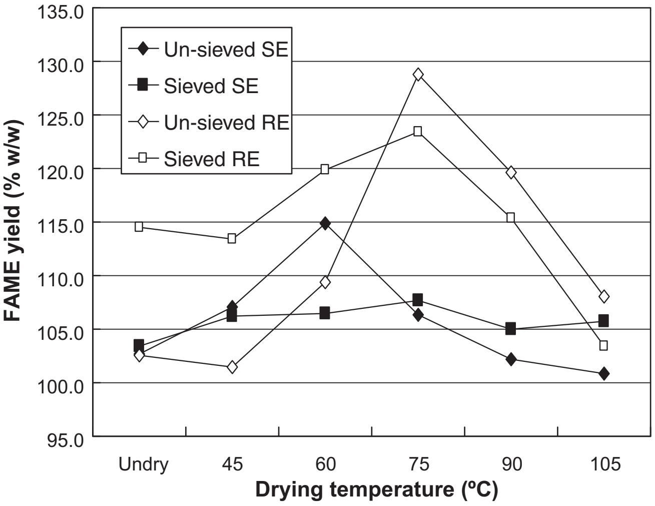

Fig. 9. FAME yield for SE and RE processes at different drying temperature for sieved and un-sieved ground Jatropha seeds (de-shelled).

extraction yield for both SE and RE processes increased at a high rate until they reached the optimum temperature at 75 °C. The combination of positive extraction effects brought by the removal of moisture content and surface transformation from heat treatment was clearly reflected here. Further increment of drying temperature resulted in loss of extracts due to overheating which potentially lead to surface destruction. Besides providing a higher extraction yield than SE, RE also registered a lower extraction loss at higher drying temperatures. This again proven that RE process had a higher tolerance and less sensitivity towards high temperature pre-treatment processes. This is vital in order for the extraction process to take advantage of the benefit of heat treatment at higher drying temperature. Meanwhile, sieved ground Jatropha seeds were found to have lower extraction yield than their un-sieved counterparts especially at higher drying temperatures. This might be due to the fact that sieving of de-shelled ground seeds had a higher probability of removing certain extract-rich portions from the core of the seeds. Nevertheless, sieved ground seeds had a more stable extraction yield due to more uniformity in the particle size.

Fig. 9 shows the FAME yield for un-sieved and sieved ground Jatropha seeds for SE and RE at 12 h drying duration. Effect of increasing drying temperature on FAME yield for SE process seemed to be negligible for sieved ground seeds. For un-sieved ground seeds, FAME yield exhibited an optimum at 60 °C and was higher than sieved ground seeds which had been explained previously. Even though extraction yield for un-sieved ground seeds undergoing SE process varied greatly, FAME yield did not follow similar trend possibly due to maximum extractable amount of fatty acids had been reached. On the other hand for RE process, both un-sieved and sieved ground seeds contained an optimum FAME yield at 75 °C. This was similar to the optimum point for the extraction efficiency shown in Fig. 8. After the optimum point, FAME yield dropped drastically with increasing drying temperature at higher decrement compare to those shown in Fig. 6. This was understandable since decorticated ground seeds will have a larger exposure to the heat treatment condition due to their higher surface area per volume. Thus, destruction of biomass surface might be more rampant and more obstructive to the fatty acids extraction.

3.5. Optimization of solid pretreatment conditions

Table 1 shows the solid pretreatment prerequisites while Table 2 listed the maximum responses for extraction and FAME yields for both SE and RE processes matching the conditions in Table 1. Drying temperatures of 45 °C and 60 °C were categorized as low temperature while 75 °C, 90 °C and 105 °C were grouped as high drying temperature. All of the responses in Table 2 were obtained from drying duration of 12 h unless being specified otherwise. Almost all of the responses from supercritical reactive extraction were higher than their corresponding conventional two-step extraction and transesterification process with increment up to 22.1% for extraction yield and 56.0% for FAME yield (Code 4). For grounded seeds with shell, the highest extraction and FAME yield were 64.03% w/w and 108.51% w/w respectively (Code 3). Decorticated ground seeds can hardly provide any improvement in terms of extraction yield (roughly 7.0%). However, FAME yield was increased by 18.7% due to the removal of shell. This proved that the absence of hard cover shell can promote extraction of fatty acids (triglycerides and free fatty acids) and would be important for biodiesel production to increase FAME yield. Virgin ground Jatropha seeds were found to have the lowest extraction yield

Table 1
Codes for various solid pretreatment conditions.

Solid pretreatment (grounded)											
With shell						De-shelled					
Dry				Undry		Dry				Undry	
Low temp		High temp				Low temp		High temp			
Sieved	Un-sieved	Sieved	Un-sieved	Sieved	Un-sieved	Sieved	Un-sieved	Sieved	Un-sieved	Sieved	Un-sieved
1	2	3	4	5	6	7	8	9	10	11	12

Table 2
Optimum value for each response under the stipulated pretreatment conditions.

Code	Extraction yield (% w/w)		FAME yield (% w/w)	
	RE	SE	RE	SE
1	58.23	52.53	103.71	82.94
2	43.15	46.53	80.65[a]	60.98
3	64.03[a]	53.46	108.51	88.75
4	51.37	42.07	100.37	64.33
5	54.31	48.58	83.69	80.50
6	38.63	35.71	70.91	59.66
7	63.68	63.50	119.88	106.46
8	66.61	61.35	109.42	114.87
9	64.49	64.83	123.36	107.71
10	68.50	66.82	128.78	106.38
11	62.44	60.83	114.57	103.47
12	57.69	53.39	102.54	102.72

[a] Drying duration of 24 h.

and FAME yield which emphasized the need to undergo solid pretreatment processes. Sieving them to smaller particle size fraction (⩽1.0 mm) proved to be more effective than subjecting them for heat treatment as the increment of extraction and FAME yield were slightly larger. Higher heat treatment temperature was beneficial compare to lower heat treatment temperature provided that the optimum temperature for the seeds was not breached which might lead to over-heating. Lastly, RE process was extremely helpful to close the gap between the optimum yields of different solid pretreatment processes as demonstrated in this study. For example, SE FAME yield for grounded seeds drying at low temperature and un-sieved exhibited only 60.98% w/w compare to drying at high temperature and sieved at 88.75% w/w. When subjected to supercritical reactive extraction, FAME yield was increased to 80.65% w/w without the need for additional solid pretreatments such as drying at high temperature or sieving. Thus, this had a high potential to save additional cost and energy requirements especially for process intensification of biodiesel production.

4. Conclusion

In this study, several conclusions can be drawn from the results and observations discussed above. Firstly, moisture content play a significant role in the oil extraction of grounded Jatropha seeds only at lower drying temperature. Even though more moisture were being removed at higher drying temperature, extraction and FAME yield still registered drastic drop due to the possibility of biomass surface changes from the high temperature heat treatment. Secondly, extraction yield and FAME yield were not directly proportional in some cases especially at high drying temperatures. Extraction yield could increase due to higher amount of lipids being extracted out but the total amount of fatty acids might remain the same and vice versa. Lastly, although solid pretreatments for biomass such as grounded Jatropha seeds are important especially in optimization of extraction and FAME yield, they are invariably time-consuming and incur additional costs both in terms of capital and operational. As had been shown in the experimental study in this work, supercritical methanol extraction and transesterification has the ability to reduce the decrement of extraction and FAME yield due to the skipping of several key pretreatment processes such as drying and sieving. This will surely add a new dimension for both operational and economic considerations to process intensification of biodiesel production from oil-seeds biomass such as *J. curcas* L. in the future.

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References

[1] S. Lim, K.T. Lee, Recent trends, opportunities, challenges of biodiesel in Malaysia: an overview, Renew. Sustain. Energy Rev. 14 (3) (2010) 938–954.
[2] N. Foidl, G. Foidl, M. Sanchez, M. Mittelbach, S. Hackel, *Jatropha curcas* L. as a source for the production of biofuel in Nicaragua, Bioresour. Technol. 58 (1) (1996) 77–82.
[3] D. Srinivas, J. Satyarthi, Biodiesel production from vegetable oils and animal fat over solid acid double-metal cyanide catalysts, Catal. Surveys Asia (2010) 1–16.
[4] X. Deng, Z. Fang, Y.H. Liu, Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process, Energy Convers. Manage. 51 (12) (2010) 2802–2807.
[5] S.A. El Sherbiny, A.A. Refaat, S.T. El Sheltawy, Production of biodiesel using the microwave technique, J. Adv. Res. 1 (4) (2010) 309–314.
[6] S. Jain, M.P. Sharma, Biodiesel production from *Jatropha curcas* oil, Renew. Sustain. Energy Rev. 14 (9) (2010) 3140–3147.
[7] S. Saka, D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2) (2001) 225–231.
[8] Z. Ilham, S. Saka, Two-step supercritical dimethyl carbonate method for biodiesel production from *Jatropha curcas* oil, Bioresour. Technol. 101 (8) (2010) 2735–2740.
[9] C.H. Chen, W.H. Chen, C.M.J. Chang, I. Setsu, C.H. Tu, C.J. Shieh, Subcritical hydrolysis and supercritical methylation of supercritical carbon dioxide extraction of Jatropha oil, Sep. Purif. Technol. 74 (1) (2010) 7–13.
[10] S.H. Shuit, K.T. Lee, A.H. Kamaruddin, S. Yusup, Reactive extraction of *Jatropha curcas* L. seed for production of biodiesel: process optimization study, Environ. Sci. Technol. 44 (11) (2010) 4361–4367.
[11] K.J. Harrington, C. D'Arcy-Evans, Transesterification in situ of sunflower seed oil, Ind. Eng. Chem. Prod. Res. Dev. 24 (2) (1985) 314–318.
[12] J. Qian, F. Wang, S. Liu, Z. Yun, In situ alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal, Bioresour. Technol. 99 (2008) 9009–9012.
[13] S. Lim, S.S. Hoong, L.K. Teong, S. Bhatia, Supercritical fluid reactive extraction of *Jatropha curcas* L. seeds with methanol: a novel biodiesel production method, Bioresour. Technol. 101 (18) (2010) 7169–7172.
[14] D. Shankar, Y.C. Agrawal, B.C. Sarkar, B.P.N. Singh, Enzymatic hydrolysis in conjunction with conventional pretreatments to soybean for enhanced oil availability and recovery, JAOCS J. Am. Oil Chem. Soc. 74 (12) (1997) 1543–1547.
[15] V. Kochergin, K. Miller, Evaluation of target efficiencies for solid–liquid separation steps in biofuels production, Appl. Biochem. Biotechnol. 163 (1) (2011) 90–101.
[16] H. Mazaheri, K.T. Lee, S. Bhatia, A.R. Mohamed, Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: an optimisation study using response surface methodology, Bioresour. Technol. 101 (23) (2010) 9335–9341.
[17] W.M.J. Achten, L. Verchot, Y.J. Franken, E. Mathijs, V.P. Singh, R. Aerts, et al., Biomass Bioenergy 32 (12) (2008) 1063–1084.
[18] G.M. Gübitz, M. Mittelbach, M. Trabi, Exploitation of the tropical oil seed plant *Jatropha curcas* L., Bioresour. Technol. 67 (1) (1999) 73–82.
[19] P. Sirisomboon, P. Kitchaiya, Physical properties of *Jatropha curcas* L. kernels after heat treatments, Biosyst. Eng. 102 (2) (2009) 244–250.
[20] M. Kashaninejad, A. Mortazavi, A. Safekordi, L.G. Tabil, Thin-layer drying characteristics and modeling of pistachio nuts, J. Food Eng. 78 (1) (2007) 98–108.
[21] R.N. Singh, D.K. Vyas, N.S.L. Srivastava, M. Narra, SPRERI experience on holistic approach to utilize all parts of *Jatropha curcas* fruit for energy, Renew. Energy 33 (8) (2008) 1868–1873.
[22] L.F. Gutiérrez, C. Ratti, K. Belkacemi, Effects of drying method on the extraction yields and quality of oils from Quebec sea buckthorn (*Hippophaë rhamnoides* L.) seeds and pulp, Food Chem. 106 (3) (2008) 896–904.
[23] W.H. Chen, H.C. Hsu, K.M. Lu, W.J. Lee, T.-C. Lin, Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass, Energy 36 (5) (2011) 3012–3021.